

## PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference TS 1214 PCT	FOR FURTHER ACTION <small>See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)</small>	
International application No. PCT/EP 03/50908	International filing date (day/month/year) 28.11.2003	Priority date (day/month/year) 28.11.2002
International Patent Classification (IPC) or both national classification and IPC B01D53/14		
<b>Applicant</b> <b>SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
 

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.
3. This report contains indications relating to the following items:
  - I  Basis of the opinion
  - II  Priority
  - III  Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV  Lack of unity of invention
  - V  Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI  Certain documents cited
  - VII  Certain defects in the international application
  - VIII  Certain observations on the international application

Date of submission of the demand 14.06.2004	Date of completion of this report 18.02.2005
Name and mailing address of the International preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Faria, C Telephone No. +31 70 340-3541



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/50908

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

### Description, Pages

1-12 as originally filed

### Claims, Numbers

2-13 as originally filed  
1 filed with telefax on 25.11.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	1-13
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-13
Industrial applicability (IA)	Yes: Claims	1-13
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

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**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1) Reference is made to the following documents:

- D1: GB-A-2 275 625 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B. V.) 7 September 1994 (1994-09-07)
- D2: US-A-3 725 531 (PEARSON ET AL) 3 April 1973 (1973-04-03)
- D3: GB-A-2 103 645 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B. V.) 23 February 1983 (1983-02-23)
- D4: US-A-4 145 192 (BEISE ET AL) 20 March 1979 (1979-03-20)
- D5: US-A-3 826 811 (HAKKA) 30 July 1974 (1974-07-30)

2) The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claim 1 does not involve an inventive step in the sense of Article 33(3) PCT.

2.1) The document D1 is regarded as being the closest prior art to the subject-matter of claim 1, and discloses (the references in parentheses applying to this document): a process for removing hydrogen sulphide and organic sulphur compounds, such as mercaptans and carbonyl sulphide from gas, such as natural gas comprising the following steps:

- a) contacting the gas in an absorber with a regenerable aqueous absorbent;
- b) contacting the treated gas from step a) with a solid adsorbent.

A suitable absorbent for use in step a) is an aqueous solution of di-isopropanol amine sulfolane (page 1 lines 15-18).

Suitable solid adsorbents for use in step b) are molecular sieves, especially zeolites of the type 5A and 13X (page 2 lines 6-8).

Up to about 95% of mercaptans present in the gas is removed in step a) (page 1, lines 19-21), while step b) provides at least a 98% removal of mercaptans (page 2, line 5).

2.2) The significant difference between the subject matter of claim 1 and D1 is that D1 does not specify the relative amounts of the components of the absorbent used in step a) while claim 1 specifies that the adsorbent (aqueous washing solution) comprises 10-45 wt% of a physical adsorbent and 20-60 wt% of an amine.

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2.3)No effect directly deriving from this difference has been demonstrated. Therefore, the objective problem solved by the present invention is the provision of an alternative aqueous washing solution in a process for the removal of hydrogen sulphide and mercaptans from a gas stream.

2.4)The use of absorbents as specified in claim 1 for the removal of hydrogen sulphides and mercaptans from gas streams is well known in the art (see D2 col. 1, lines 32-51). Furthermore, as acknowledge by the applicant and shown in D3 (page 1, lines 106-page2, line 20) and D4 (col.1, lines 28-41), the use of absorbents as specified in claim 1 for the removal of acid gas components such as hydrogen sulphide and carbon dioxide from gas streams is well known in the art.

The skilled person would therefore be aware of the relative amounts of the components normally used in the adsorbent disclosed by D1, and would arrive to a composition falling within the scope of claim 1 without the exercise of inventive skill.

3)Dependent claims 2-13 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, see document D1-D5 and the corresponding passages cited in the search report.

A M E N D E D   C L A I M S

1. A process for the removal of hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide from a gas stream comprising hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide, by removing in a first step most of the hydrogen sulphide, part of the mercaptans and optionally part or most of the carbon dioxide and carbonyl sulphide by washing the gas stream with an aqueous washing solution comprising 10 to 45 wt% based on total solution of water, 10 to 40 wt% based on total solution of a physical solvent and 20 to 60 wt% based on total solution of an amine, which first removal step is followed by a second removal step in which mercaptans are removed by means of molecular sieves, in which process the amount of mercaptans which is removed by the aqueous washing stream is between 60 and 96 % (of total removed mercaptans in steps one and two), and the amount which is removed by the mol sieves is between 40 and 4 % (of total removed mercaptans in step one and two).  
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2. A process according to claim 1, in which the total gas stream comprises 0.05 to 20 vol% hydrogen sulphide, 10 to 1500 ppmv mercaptans and 0 to 40 vol% carbon dioxide, preferably 0.1 to 5 vol% hydrogen sulphide, 20 to 1000 ppmv mercaptans and 0 to 30 vol% carbon dioxide.  
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3. A process according to claim 1 or 2, in which the total gas stream comprises hydrogen sulphide in an amount between 0.15 and 0.6 vol%.
4. A process according to any of claims 1 to 3, in which the ratio between the amount of mercaptans (expressed as

ppmv) and the amount of hydrogen sulphide (expressed as vol%) is at least 50, preferably at least 100, more preferably at least 200.

5. A process according to any of claims 1 to 4, in which the gas stream is natural or associated gas.

6. A process according to any of claims 1 to 5, in which the physical solvent is sulfolane.

7. A process according to any of claims 1 to 6, in which the amine is a secondary or tertiary amine, preferably an 10 amine compound derived from ethanol amine or a mixture thereof, more preferably DIPA, DEA, MMEA, MDEA, or DEMEA, most preferably DIPA or MDEA or a mixture thereof.

8. A process according to any of claims 1 to 7, in which 15 the aqueous washing solution comprises 20 to 35 wt% based on total solution of water, 20 to 35 wt% of a physical solvent and 40 to 55 wt% of an amine.

9. A process according to any of claims 1 to 9, in which the gas stream obtained in the first step is cooled to a 20 temperature between 5 and 45 °C, preferably between 10 and 35 °C, where after any condensate is separated from the gas stream.

10. A process according to any of the preceding claims, in which the first step is carried out at a temperature of at least 20 °C, preferably between 25 and 90 °C, more 25 preferably between 30 and 55 °C, at a pressure between 15 and 90 bara.

11. A process according to any of the preceding claims, in which in the second step a crystalline molecular sieve is used, preferably a sieve having an average pore 30 diameter of 5 ångström or more, especially about 6 ångström.

12. A process according to any of the preceding claims, in which the second step is carried out at a temperature of 25 °C and a pressure between 15 and 90 bara.

5 13. A process according to any of the preceding claims in which the regeneration gas of the second step containing mercaptans is remixed with the starting gas stream or is treated in a dedicated absorber.